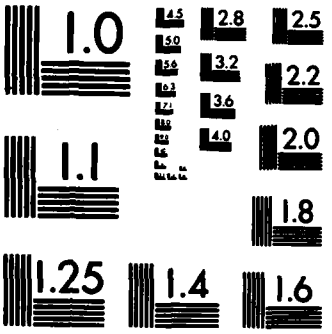
AD-A150 863 MONITORING OF LAMINATE CURE WITH MICRODIELECTROMETRY (U) MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF ELECTRICAL ENGIN... W W BIDSTRUP ET AL. 30 NOV 84 TR-2 1/1

UNCLASSIFIED N00014-84-K-0274 F/G 11/4 NL

END

FILMED

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

(2)

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-84-K-0274

Task No. NR 039-260

TECHNICAL REPORT NO. 2

Monitoring of Laminate Cure with Microdielectrometry

by

Wayne W. Bidstrup, Norman F. Sheppard, Jr.

and Stephen D. Senturia

Prepared for Presentation

at

Society of Plastics Engineers ANTEC 85

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Department of Electrical Engineering and Computer Science

and Center for Materials Science and Engineering

Cambridge, Massachusetts

April 29 - May 2, 1985

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A150863	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Monitoring of Laminate Cure with Microdielectrometry		5. TYPE OF REPORT & PERIOD COVERED Technical Report 5/1/84-11/30/84
		6. PERFORMING ORG. REPORT NUMBER Technical Report No. 2
7. AUTHOR(s) Wayne W. Bidstrup, Norman F. Sheppard, Jr., and Stephen D. Senturia		8. CONTRACT OR GRANT NUMBER(s) N00014-84-K-0274
9. PERFORMING ORGANIZATION NAME AND ADDRESS Massachusetts Institute of Technology 77 Massachusetts Avenue Cambridge, MA 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 039-260
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy, Office of Naval Research 800 N. Quincy Street Arlington, VA 22217		12. REPORT DATE 11/30/84
		13. NUMBER OF PAGES 11
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for publich release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

fiber-reinforced composite, cure monitoring, laminate, epoxy-glass composite, epoxy-graphite composite, dielectrics, microdielectrometry

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We report the use of microdielectrometry for monitoring the cure of the matrix resins in epoxy-glass and epoxy-graphite composites. The multi-ply laminates are cured in a press using ramped temperatures. The microdielectrometer sensor is embedded in a cavity made by cutting a hole in each of the inner plies. For a brominated-epoxy glass-reinforced prepreg ramped to final cure temperatures as high as 200°C and at pressure up to 60 psi, a reproducible pattern of cure events is observed beginning with the flow of

cvers

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(Cont. from 1473)

resin onto the sensor electrodes and ending with the characteristic stabilizing of the loss factor late in cure. The apparent dielectric properties (permittivity and loss factor) show good reproducibility for identically prepared samples, but their characteristics differ from those observed in neat resin. For an MY-720 based graphite prepreg, at cure temperatures below 160°C and at pressures up to 60 psi, features in the cure data are similar to what is seen in epoxy glass. However, at pressures of 60 psi and higher cure temperatures, there is evidence that the graphite fibers can touch the sensor surface and short the electrodes, a problem that will require a revised sensor package design. Keywords include: fiber-reinforced composite and cure monitoring.

MONITORING OF LAMINATE CURE WITH MICRODIELECTROMETRY

BY

WAYNE W. BIDSTRUP, NORMAN F. SHEPPARD, JR.,

AND STEPHEN D. SENTURIA

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

CAMBRIDGE, MASSACHUSETTS 02139

INTRODUCTION

Monitoring the cure of epoxy resins by measurement of the dielectric properties is a well-established technique. Conventional methods use either parallel-plate or comb-electrode structures in conjunction with a capacitance bridge [1-5]. Recently, a new system known as microdielectrometry has been developed [6,7]. It uses an integrated circuit microsensor that combines miniature comb electrodes with amplification and temperature measurement in a single probe. Microdielectrometry has already been used to monitor the cure of neat epoxy resins [6-8]. The cure of fiber-reinforced composites presents additional problems because of the presence of fibers, which may be conducting, and because the electrode system used must be compatible with the shape of the part being fabricated. This paper reports the use of microdielectrometry to monitor cure in typical composites. A method of embedding the small microdielectrometry probe into the laminate was devised, and cure measurements were performed on both glass-fiber-reinforced and graphite-fiber-reinforced laminates.

EQUIPMENT AND PROCEDURES

Microdielectrometry sensors were obtained from Micromet Instruments. The integrated circuit sensor has dimensions 2.5 x 5 mm, and is packaged in a flexible ribbon cable with overall width of about 9 mm, and a thickness of about 0.4 mm. The sensor is driven by MIT's research microdielectrometer instrument, which is functionally equivalent to a Micromet Instruments System II Microdielectrometer. This instrument measures the dielectric permittivity ε' and the dielectric loss ε'' of whatever material is in contact with the sensor's electrodes. The frequency range used in these experiments was 1 - 10,000 Hz. The sensor also includes a thermal diode which measures sample temperature.

Five-inch square laminates were made from two types of materials. The first was a circuit-board type of epoxy-glass prepreg, with a DICY-cured brominated DGEBA resin. The second was a graphite cloth with an uncatalyzed TGMDA-DDS matrix resin (Fiberite 976). The sensor was embedded into the laminate by cutting holes in the central plies just slightly larger than the sensor (Figure 1). The overall laminate thickness was designed so that the sensor would not support the full load of the platens during lamination. This corresponded to 11 plies of the glass prepreg, or 4 plies of the graphite prepreg. Cure of the laminates was done in a Carver Model 2518 hydraulic lab press (12" platens) with platen temperatures controlled by a Wizard Model 1601 controller. The typical cure sequence was to ramp the press temperature from room temperature to 177°C at 5°/min, then holding at that temperature. Lamination pressure was maintained at 60 psi throughout the cure. Total cycle time was typically two hours.

DIELECTRIC PROPERTIES

The application of an alternating electric field to a material produces a polarization response described by the complex dielectric constant. The real part of the response, called the permittivity and denoted by ε', measures the polarization that is in phase with the applied field. The imaginary part of the respose, called the dielectric loss factor and denoted by ε'', measures the out-of-phase component of the polarization, and is determined by energy dissipation in the sample during the polarization process.

The experimentally observed permittivity and loss factor include both bulk and interface effects. The bulk permittivity is determined by the orientation of molecular dipoles in the applied electric field. The bulk loss factor can include loss terms associated with dipole orientation and contributions from the bulk conductivity of the material. In the experiments reported here, the observed loss factor is completely dominated by conductivity effects; no characteristic dipolar loss peaks are observed.

The conductivity arises from ions that are always present to some degree in commercial resins. These ions may be residues of the chemical synthesis, may arise from weak-electrolyte ionization of components of the resin/curing agent mixture, or, may come from the fiber or from the fiber surface treatment.

When conductivity dominates the dielectric loss factor, there is a simple relation between loss factor and conductivity:

$$\varepsilon'' = \frac{\sigma}{\omega \varepsilon_0}$$

In this expression, σ is the conductivity in $(\text{Ohm-cm})^{-1}$, ω is the angular frequency of the measurement in rad/sec, and ε_0 is the permittivity of free space (8.85×10^{-14} Farads/cm).

The conductivity can be further expressed as

$$\sigma = \sum_i z_i q n_i \mu_i$$

where z_i is the valence of the ith ionic species, q is the electronic charge, n_i is the concentration, and μ_i is the mobility. The primary effect of cure is to restrict the motion of ions through the matrix resin (i.e., to reduce the mobility). As a result, while the conductivity increases with increasing temperature, it decreases with increasing extent of cure. This means that during a ramped cure of a partially staged resin or prepreg, one sees, first, an increase in conductivity as the resin melts and flows, and later, a decrease in conductivity as the cure proceeds toward completion.

There is an important interface effect that is observed in most resin-cure experiments. It is the polarization of the electrodes due to the buildup of ions at blocked electrodes [9]. This effect is observed whenever the conductivity is large enough and the frequency low enough to permit observable charging of the electrode blocking layer during one cycle of the ac waveform. The primary experimental effect of blocking layer polarization is that the experimental value of ε' is much greater than the true bulk value. A secondary effect, which occurs only when polarization is significant, is a reduction of the experimental value of ε'' from its true bulk value. A quantitative model of polarization effects is demonstrated in [9].

Electrode polarization effects were observed in the experiments described here, particularly at the lower frequencies. The full analysis of these effects will be the subject of a future publication. The data presented here will emphasize those results in which the effects of electrode polarization can be ignored. Thus, we present only loss factor data (rather than permittivity), and in the discussion, emphasize the results at the higher frequencies where polarization effects are absent.

EXPERIMENTAL RESULTS

Figure 2 illustrates the loss factor versus time for a typical cure of a glass fiber reinforced prepreg. Measurements at 1, 10, 100, 1000, and 10000 Hz are made in succession as cure proceeds. Initially, the sensor is resting in a cavity surrounded by air, with no resin in contact with the electrodes. As a result, the measured loss factor is small, and the instrument indicates a minimum (or default) value at all frequencies. At about 10 minutes into the ramp, hence at a temperature of about 70°C, a noisy but dramatic increases in loss factor occurs, signifying the melt and flow of the resin onto the sensor surface. At about 18 minutes, coverage of the sensor is complete, and the quantitative measurement of resin loss factor begins. The lowest frequencies go rapidly off scale, while the higher frequencies remain on scale. Note the parallel behavior of curves at difference frequencies, indicative of conductivity-dominated behavior. All curves reach a peak at about 25 minutes, which corresponds to the end of the temperature ramp. At this point, the temperature is held constant, and the loss factor decreases due to cure.

Figure 3 illustrates the reproducibility of the loss factor measurements. Two independently prepared samples of glass reinforced prepreg were monitored by different sensors. The first sample was cured, the press was water cooled to just below room temperature, and then the second sample was cured. The data for both cure runs are plotted at two frequencies. The irregular differences early in cure can be attributed to differing details during the initial flow and electrode coverage portion of the cycle, and the slight shift between the two maxima is attribut-

able to slightly cooler starting temperatures for the platens in the second run. However, once the hold temperature is reached, the results of the two runs are nearly identical.

The frequency dependence of ε'' can be used to extract the value of conductivity. Figure 4 shows the ε'' measured at the end of cure for a glass-epoxy laminate compared with the corresponding ε'' values taken from a cure of neat resin which had been flaked from a sample of the glass-epoxy prepreg, placed on the sensor, and run through the same temperature cycle as the laminate (but with no applied pressure). It is interesting to note that the frequency dependence of ε'' in both cases is close to the $1/\omega$ behavior one would expect for a conductivity-dominated ε'', and that the ε'' value in the laminate is a factor of 10 larger than that of the neat resin. The conductivity values corresponding to these data are 6.9×10^{-9} $(\text{Ohm cm})^{-1}$ for the laminate resin, and 7.2×10^{-10} $(\text{Ohm-cm})^{-1}$ for the neat resin. We do not yet understand the reason the difference between the two measured conductivities, a result which has been reproduced several times. One possibility is that when the laminate is cured, additional ions leach out of the glass fiber or out of a surface treatment layer on the glass fiber. Another possibility is that the glass fibers are sufficiently conductive at the cure temperature to contribute to ε''. A third possibility is that interface effects between the matrix resin and the glass fiber lead to enhanced measured ε''. Identification of the origin of this difference is a subject of current study. An important implication of this result is that great care must be used in attempting to use results obtained from neat resins to predict electrical behavior of composites.

Cure studies have also been carried out on the graphite fiber reinforced laminates, although some significant practical difficulties were also encountered. Because the fibers themselves are highly conductive, direct contact between a fiber and the electrodes can short out the sensor, making the measurement inoperative. While this did occur in some lay-ups, in most cases the slightly raised facing of the sensor package held the fibers off the electrodes, so that electrode shorting due to fibers did not occur. However, an interesting adhesion interaction between the TGMDA-DDS matrix resin and the sensor and package materials was observed, which resulted in a delamination of the resin from the surface of the sensor during some runs, with an accompanying loss of measurement integrity. A similar effect has been observed by Sanjana [10]. To test whether the adhesion loss was due to the fibers or to the resin, some unreacted resin was squeezed from the graphite prepreg using the press. This resin was placed on the surface of the sensor, and the device was exposed to the normal temperature ramp. Shortly after the resin liquified, it was observed to adhere selectively to the Kapton sensor package, spontaneously delaminating from the surface of the sensor and moving under the influence of surface tension entirely onto the package. The implication is that during an experiment in a laminate, there is a tendency for

the resin to leave the sensor surface. The force of the press opposes this delamination. However, the detailed package design, in which the graphite fibers are suspended above the electrode region by the edge of the Kapton package, may actually be contributing to the adhesion loss by supporting the fibers which lift the resin off the electrodes. More work in this area is required.

A suggested test for whether the resin has delaminated is the meaured permittivity [10]. Even partial lamination will result in a drop in ε' from its nominal value at the end of cure (5 in these experiments) toward a value of 1 (air). Based on this criterion, and in spite of the experimental difficulties, several excellent runs were obtained in graphite, as illustrated in Figure 5. The behavior of the data early in cure is more complex than that obtained from the glass-epoxy system, and is not understood in detail. Toward the end of cure, however, the characteristic decrease in the ε'' values to a stable endpoint, and the ε'' frequency dependence suggestive of conductivity-dominated behavior are observed.

SUMMARY AND CONCLUSION

Microdielectrometry has been shown to offer a simple and effective method of monitoring the cure in epoxy-glass laminates, although further improvements in experimental lay-up techniques to improve reproducibility early in cure are needed. The presence of the glass fibers appears to increase the conductivity of the matrix resin over that obtained from a cure of resin flaked from the prepreg prior to cure, suggesting a direct contribution of the glass to the overall conductivity. Preliminary cure results have also been obtained in graphite-epoxy laminates, although new experimental techniques must be found to improve the integrity of the sensor/resin interface during cure.

ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Research. The authors wish to thank Paul Kyle of Polyclad for providing samples of the glass-epoxy prepreg, and Deborah Hadad of Lockheed Missiles & Space for providing samples of the graphite-epoxy prepreg. The assistance of Michael Coln of MIT in the early phases of this work, as well as many useful technical discussions with David Day of Micromet Instruments and Zal Sanjana of Westinghouse are gratefully acknowledged.

REFERENCES

1. J. Delmonte, "Electrical properties of epoxy resins during polymerization", J. of Appl. Polymer Sci., 2, 108 (1959).

2. V. Adamec, "Electrical properties of an epoxy resin during and after curing", J. Polymer Sci., 10, 1277 (1972).

3. Z. Sanjana and J. Day, "The use of dielectric analysis to characterize composite prepreg and cure", Polymer Preprints (ACS), 22, 255 (1981).

4. W. Zukas, W. McKnight, and N. Schneider, "Dynamic mechanical and dielectric properties of an epoxy resin during cure", Chemorheology of Thermosetting Polymers, ACS Symposium Series, 227, 223 (1983).

5. A. Soualmia, C. Huraux, and B. Despax, "Relation entre les parametres dielectriques et la cinetique de reaction de polymerization en phase liquide", Makromol. Chem., 183, 1803 (1982).

6. N. Sheppard, D. Day, H. Lee, and S. Senturia, "Microdielectrometry", Sensors and Actuators, 2, 263 (1982).

7. S. Senturia, N. Sheppard, H. Lee, and D. Day, "In-situ measurement of the properties of curing systems with microdielectrometry", J. Adhesion, 15, 69 (1982).

8. N. Sheppard, M. Coln, and S. Senturia, "A dielectric study of the time-temperature-transformation (TTT) diagram of DGEBA epoxy resins cured with DDS", Proc. 29th SAMPE Symposium, Reno, NV, April 1984, p. 1243.

9. D. Day, T.J. Lewis, H. Lee, and S. Senturia, "The role of boundary layer capacitance at blocking electrodes in the interpretation of dielectic cure data in adhesives", J. of Adhesion, 17, in press.

10. Z. Sanjana, private communication.

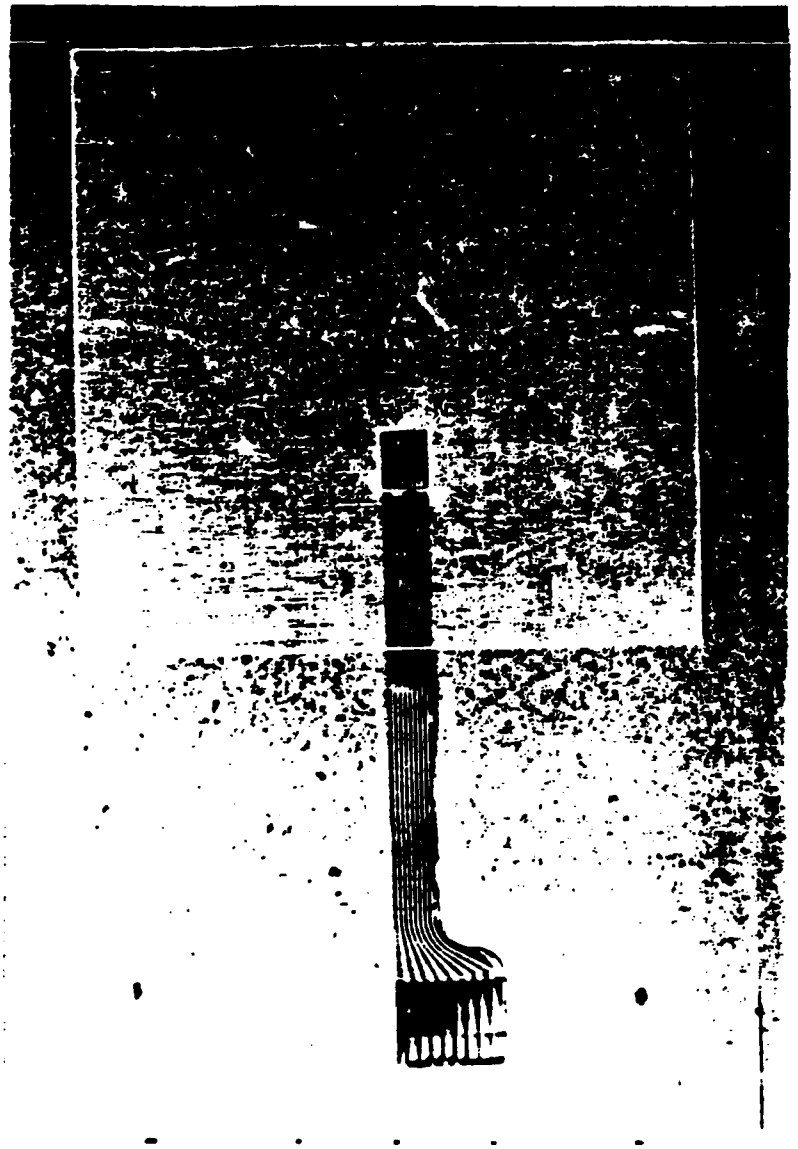


Figure 1. Microdielectrometer sensor in layed up glass-fiber reinforced prepreg prior to cure.

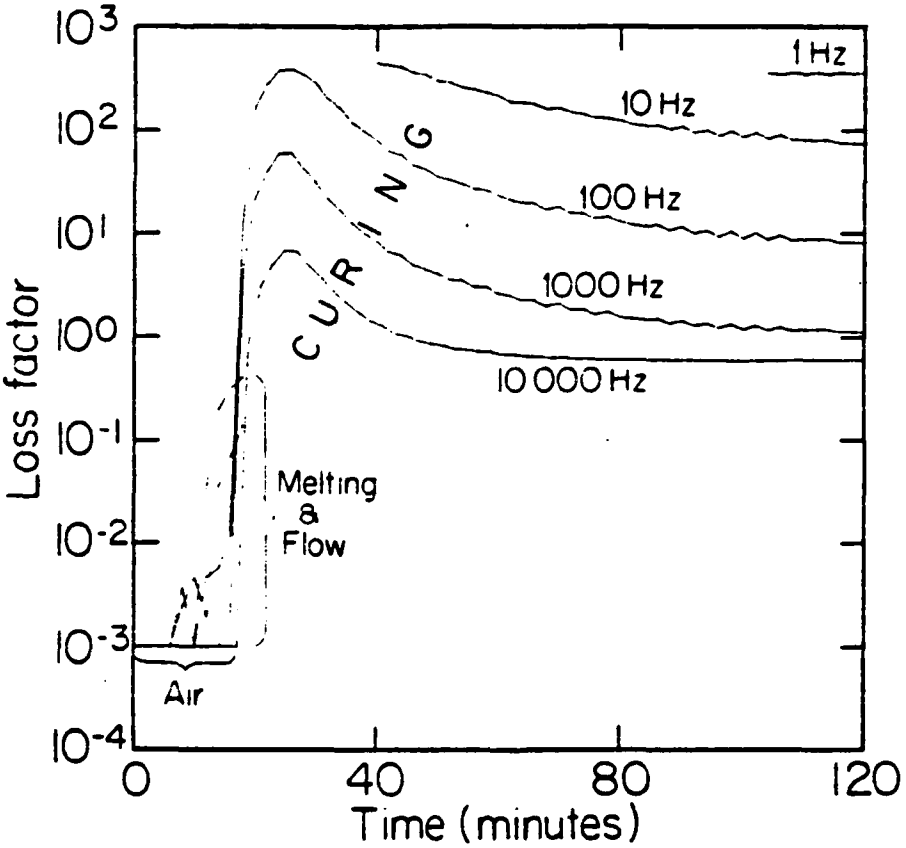


Figure 2. Loss factor vs cure time for a glass-fiber reinforced prepreg at 5 frequencies.

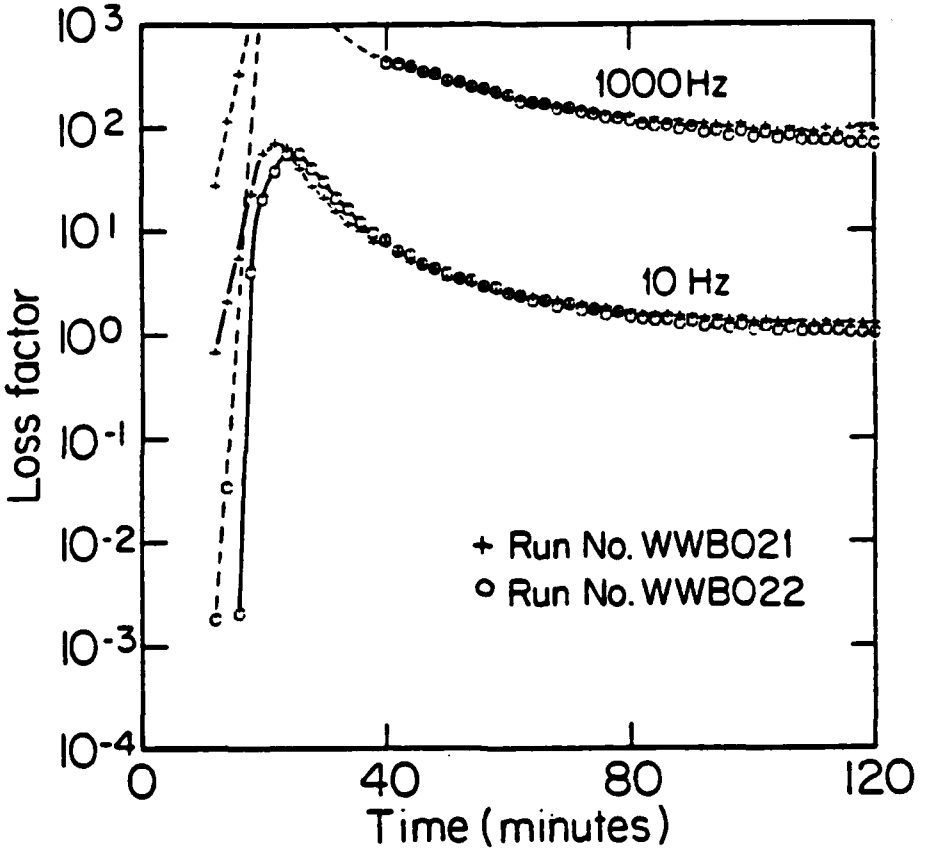


Figure 3. Reproducibility of loss factor vs cure time for glass-fiber reinforced prepreg.

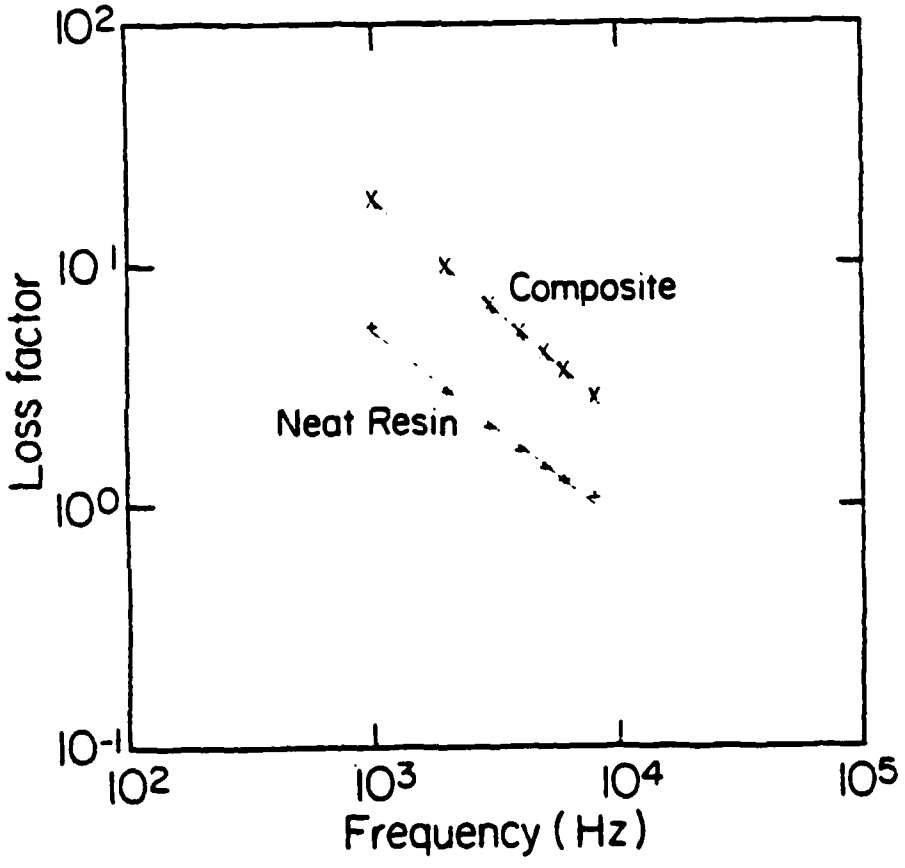


Figure 4. Comparison of loss factor vs frequency of cured neat resin and cured composite containing the same resin.

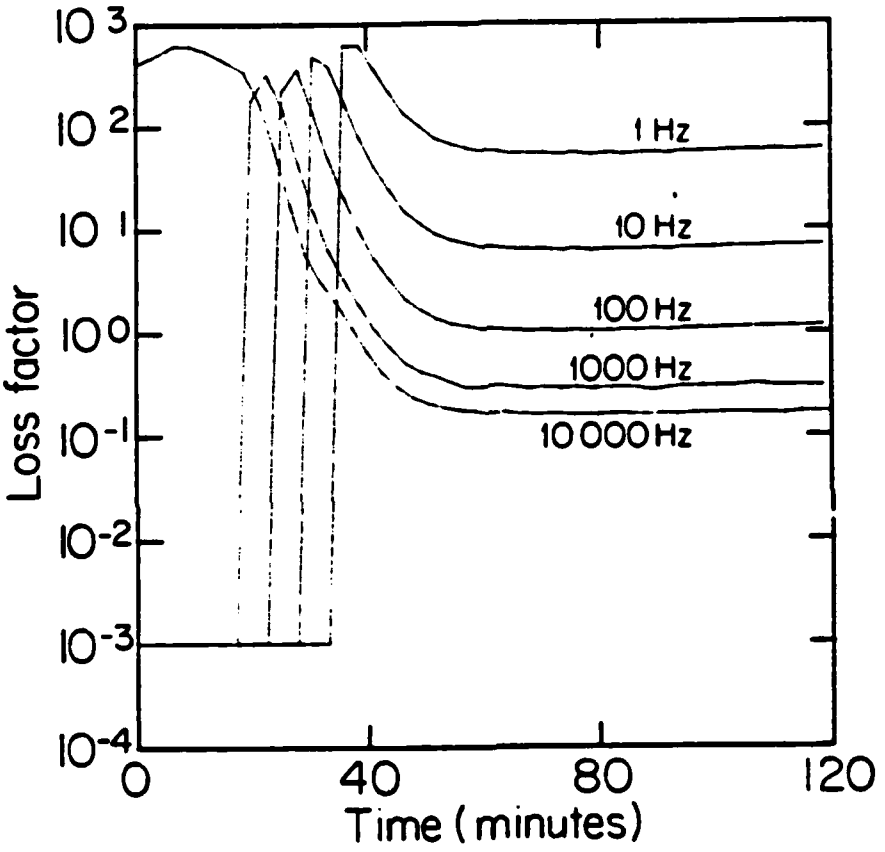


Figure 5. Loss factor vs cure time for graphite-fiber reinforced prepreg.

END

FILMED

4-85

DTIC